

NERL Report of Non-Targeted PFAS Results to NC DEQ

August 28, 2017

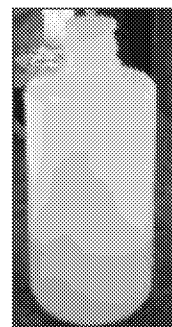
**U.S. EPA
Research Triangle Park, NC
Room C111-A/B**



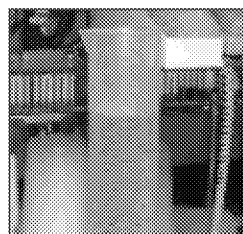
Introduction/Background

- NERL in collaboration with NCSU has been conducting PFAS research in the Cape Fear River for the last 10 years (Nakayama et al., 2007)
- Recent work based on non-targeted analysis identified a range of new PFAS (~15) from two broad families – Gen X and Nafion in Cape Fear and drinking water (Strynar et al., 2015)
- GenX was measured in drinking water mean conc. 631 ng/L (Sun et al., 2016)
- Local press picks up Sun et al., 2016 findings
- NC DEQ, R4, & NERL partner to monitor effectiveness of source remediation
- NC DEQ conducts sampling in Cape Fear over 8 weeks at 13 locations including Chemours outfall, upstream, down stream, well, source, drinking water
- NERL has provided three prior reports giving GenX results
- Today is the first report that includes non-targeted analyte results

Sample Processing Nakayama et al., 2009



1 L HDPE bottles
5 mL 1:1 HNO₃ (35%):DI
Shipped ambient



Pour water out
of sample
bottle for
volume
measurement



Wash bottle with 10
mL MeOH, add water
back to bottle, add IS
Shake



Filter entire contents
Whatman GF/A 1.7 um

All samples
Treated same
way

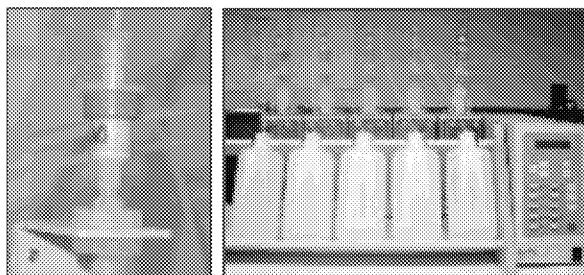
- Trip Spike
- Blanks
- Unknowns
- Calibration



Add filtered water back into
original bottle



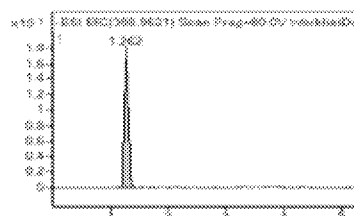
Subsample 500 mL
Store 500 mL



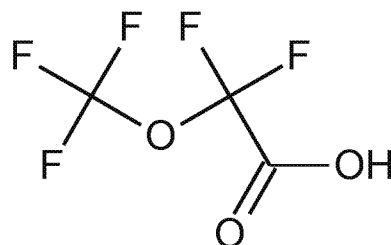
Load onto SPE tube
Waters Plus style WAX

Non-Targeted Methods

- High resolution mass spectrometry allows one to observe an unknown compound as a peak in a chromatogram and to ultimately predict the identity of this unknown
- Initially, the mass spectrometer assigns a mass for each peak observed, for example 179.9846 Daltons (Da)

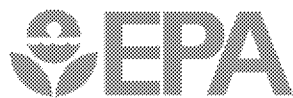


- Software then calculates the exact number and type of atoms needed to achieve that measured mass, example $C_3HF_5O_3$ (need this number and type of atoms to weigh this much)
- Software and fragmentation experiments allow determination of most likely structure:



Molecular Formula: $C_3HF_5O_3$
 Monoisotopic Mass: 179.984585 Da
 [M-H]⁻: 178.977308 Da

- With mass, formula, and structure determined, identity can be assigned by searching against databases of known compounds, example CAS number 674-13-5
- Search for standards from commercial sources to confirm identification if possible



Estimating NTA Analyte Concentration

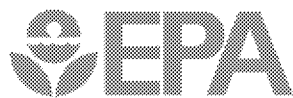
$$[NTA] = [GenX] * \frac{NTA_{PA}}{GenX_{PA}}$$

Where: **[NTA]** is the concentration of the non-targeted analysis analyte (ng/L)

[GenX] is the concentration of **GenX** (ng/L)

NTA_{PA} is the integrated peak area for the non-targeted analysis analyte

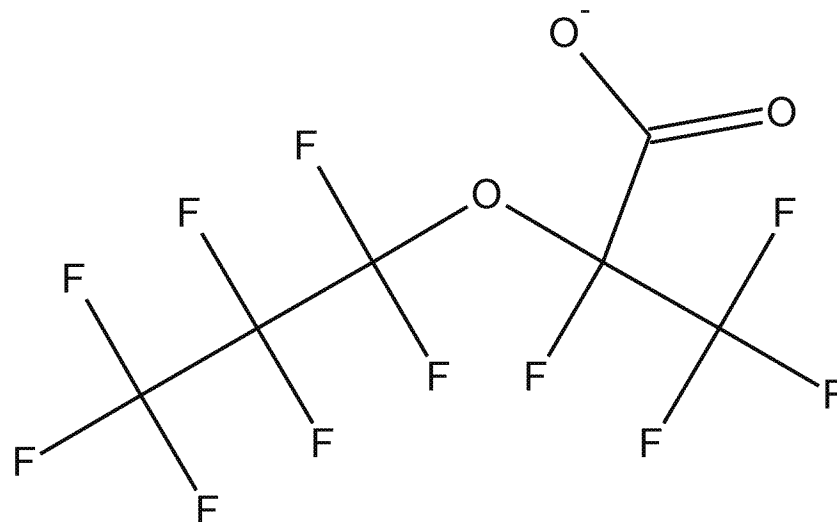
GenX_{PA} is the integrated peak area for **GenX**



Non-Targeted Analytes (NTA) Measured by LC/TOFMS Analysis

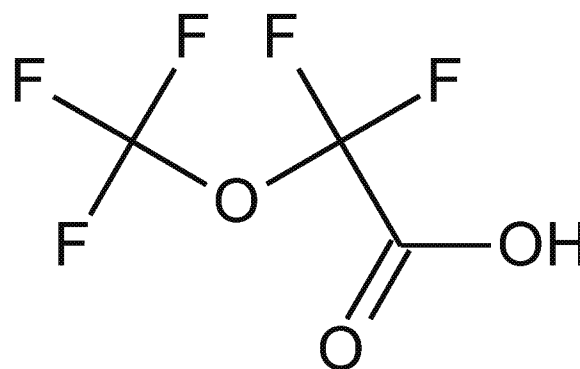
Short Name	Chemical Name	Formula	CAS no.	Monoisotopic Mass (Da)
Nafion Byproduct 1	Unknown	$C_7HF_{13}O_5S$	66796-30-3	443.9337
Nafion Byproduct 2	Unknown	$C_7H_2F_{14}O_5S$	749836-20-2	463.9399
GenX	2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)propanoic acid	$C_6HF_{11}O_3$	13252-13-6	329.9750
PFM0AA	(2,2-difluoro-2-(trifluoromethoxy)acetic acid)	$C_3HF_5O_3$	674-13-5	179.9846
PFO2HxA	perfluoro-3,5-dioxahexanoic acid	$C_4HF_7O_4$	39492-88-1	245.9763
PFO3OA	perfluoro-3,5,7-trioxaoctanoic acid	$C_5HF_9O_5$	39492-89-2	311.9680

- Class: PFECAs
- Formula: $C_6HF_{11}O_3$
- CAS no.: 13252-13-6
- Molecular Mass: 329.9750 Da
- Ref: Strynar et al., ES&T 2015;
Sun et al., 2016



PFMCAA :
(2,2-difluoro-2-(trifluoromethoxy)acetic acid)

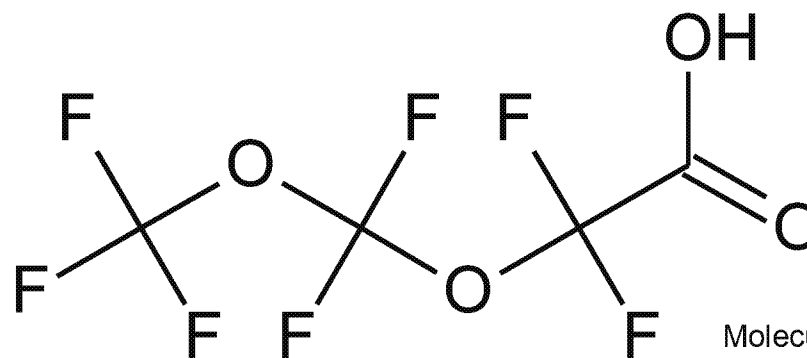
- Class: PFECAs
- Formula: $C_3HF_5O_3$
- CAS no.: 674-13-5
- Molecular Mass: 179.9846 Da
- Ref: Strynar et al., ES&T 2015;
Sun et al., 2016



Molecular Formula: $C_3HF_5O_3$
Monoisotopic Mass: 179.984585 Da
[M-H]⁻: 178.977308 Da

PFO2HxA: perfluoro-3,5-dioxahecanoic acid

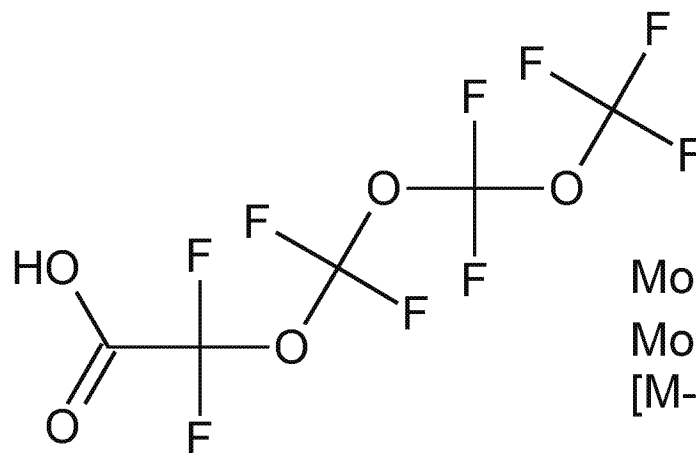
- Class: PFECAs
- Formula: $C_4HF_7O_4$
- CAS no.: 39492-88-1
- Molecular Mass: 245.9763 Da
- Ref: Strynar et al., ES&T 2015;
Sun et al., 2016



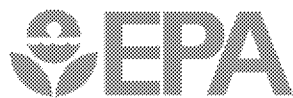
Molecular Formula: $C_4HF_7O_4$
 Monoisotopic Mass: 245.976306 Da
 [M-H]⁻: 244.969029 Da

PFO3OA: perfluoro-3,5,7-trioxaoctanoic acid

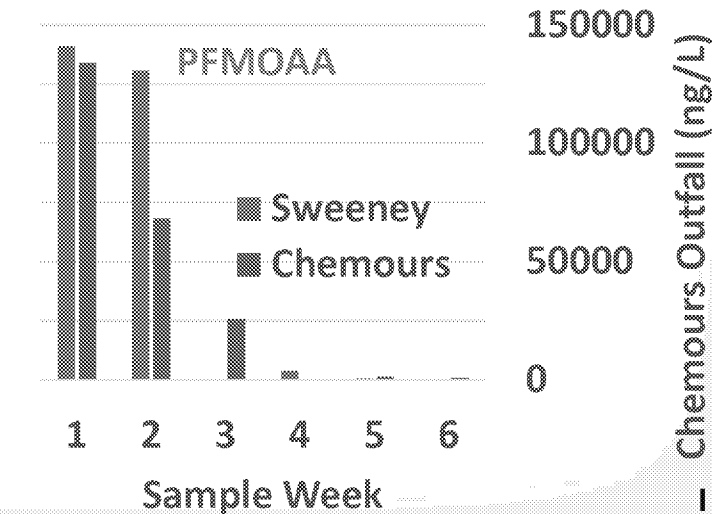
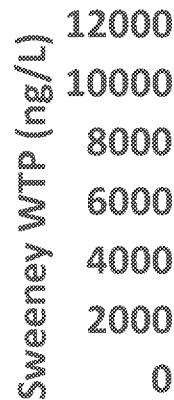
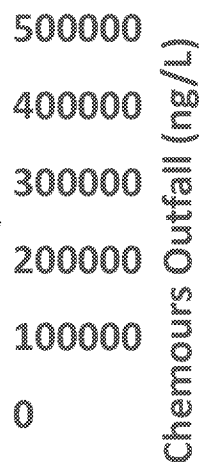
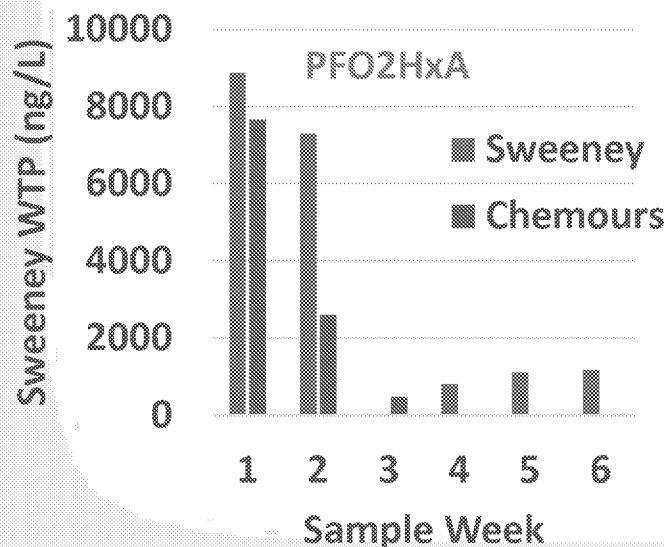
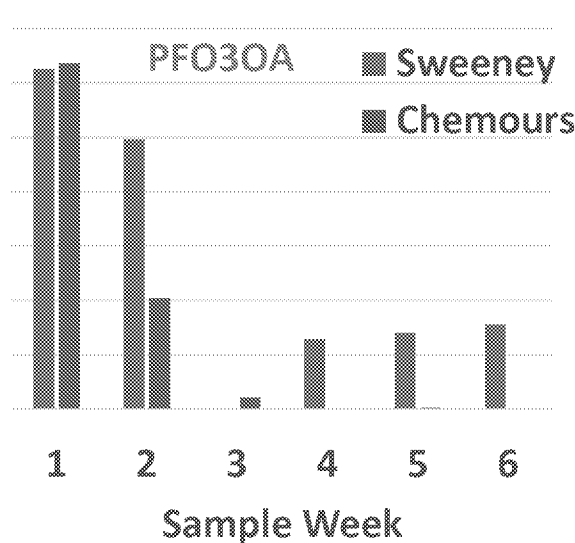
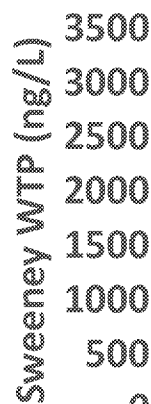
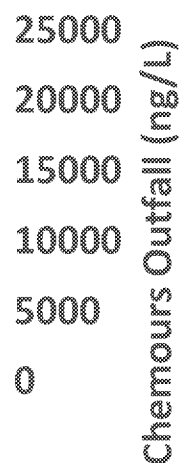
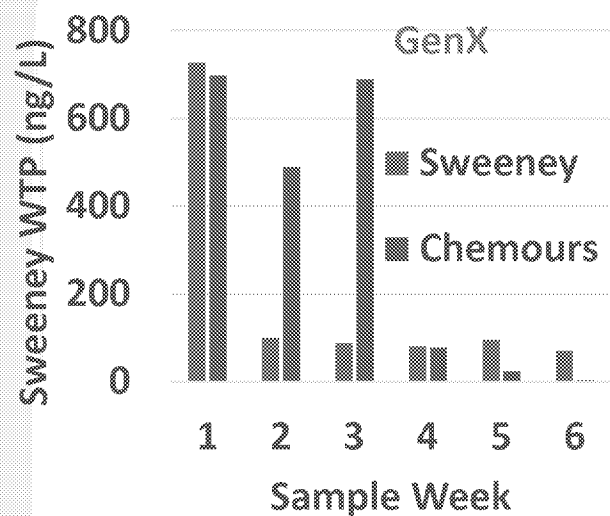
- Class: PFECAs
- Formula: $C_5HF_9O_5$
- CAS no.: 39492-89-2
- Molecular Mass: 311.9680 Da
- Ref: Strynar et al., ES&T 2015;
Sun et al., 2016



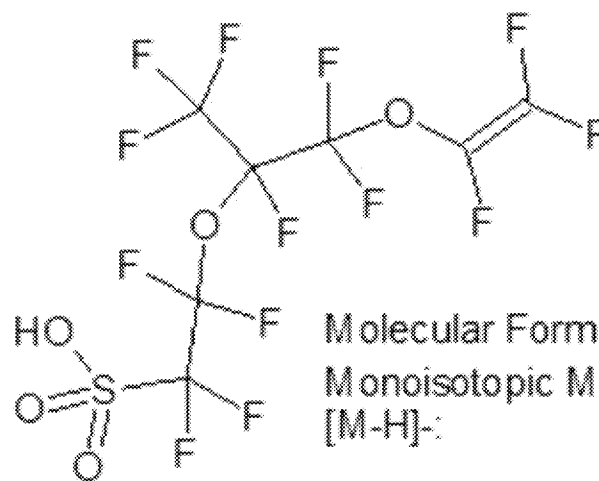
Molecular Formula: $C_5HF_9O_5$
 Monoisotopic Mass: 311.968027 Da
 [M-H]⁻: 310.96075 Da



GenX Profile Results



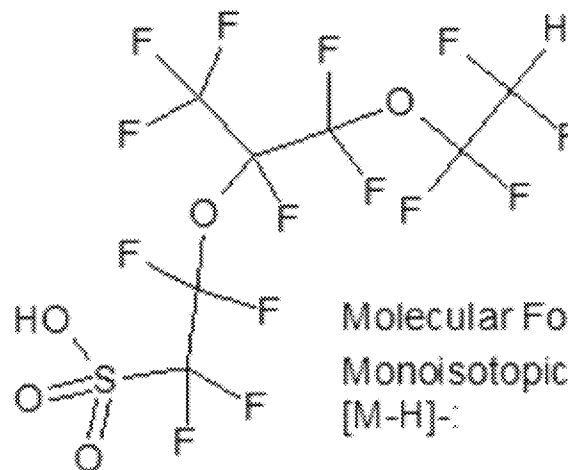
- Class: PFESAs
- Formula: $C_7HF_{13}O_5S$
- CAS no.: 66796-30-3 (for polymer)
- Monoisotopic Mass: 443.9337 Daltons
- Ref: Strynar et al., ES&T 2015



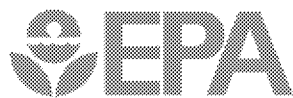
Molecular Formula: $C_7HF_{13}O_5S$
 Monoisotopic Mass: 443.9337 Da
 $[M-H]^-$: 442.9264 m/z

Nafion Byproduct 2

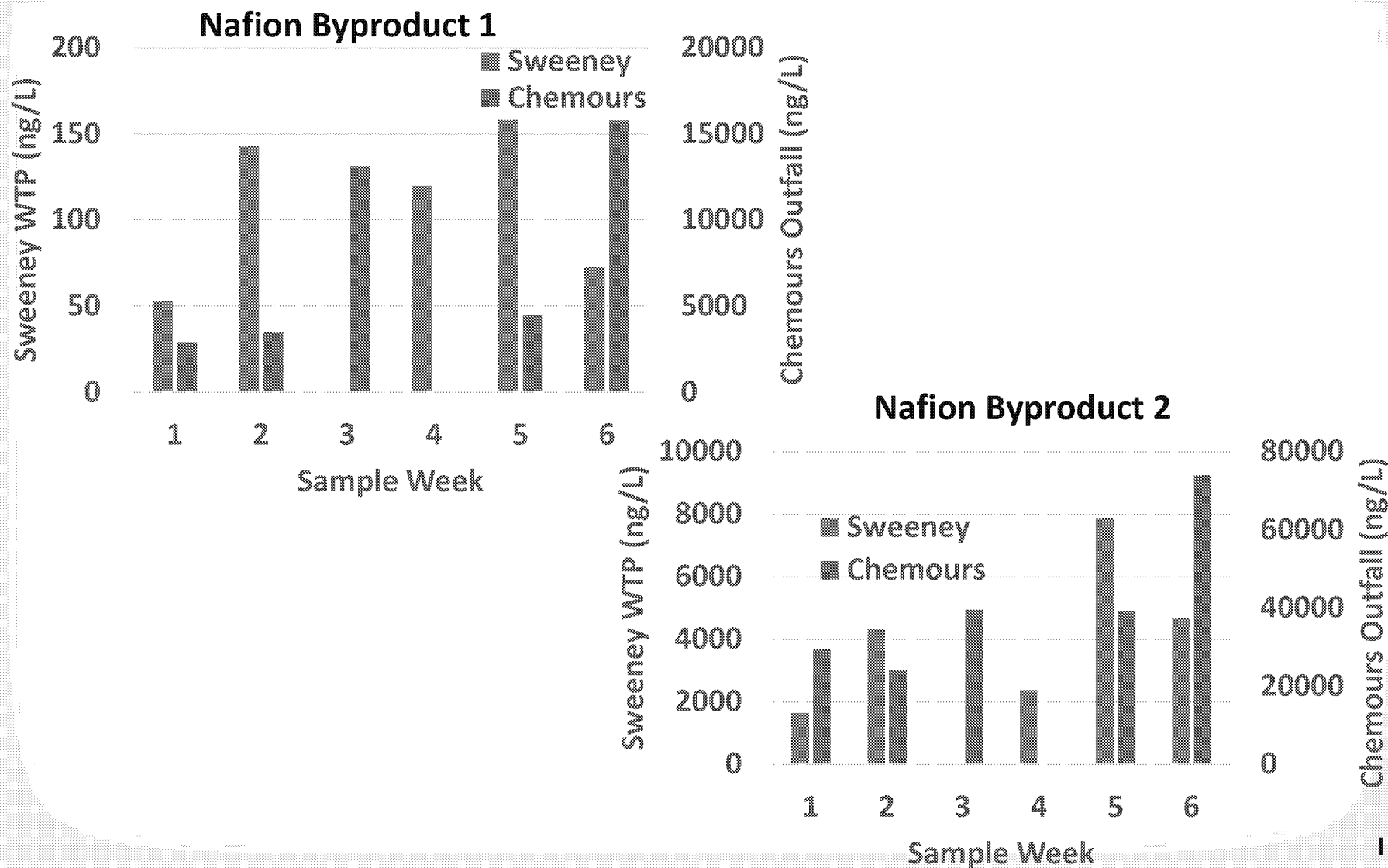
- Class: PFESAs
- Formula: $C_7H_2F_{14}O_5S$
- CAS no.: 749836-20-2
- Monoisotopic Mass : 463.9399 Da
- Ref: Strynar et al., ES&T 2015



Molecular Formula: $C_7H_2F_{14}O_5S$
 Monoisotopic Mass: 463.9399 Da
 [M-H]⁻: 462.9326 m/z

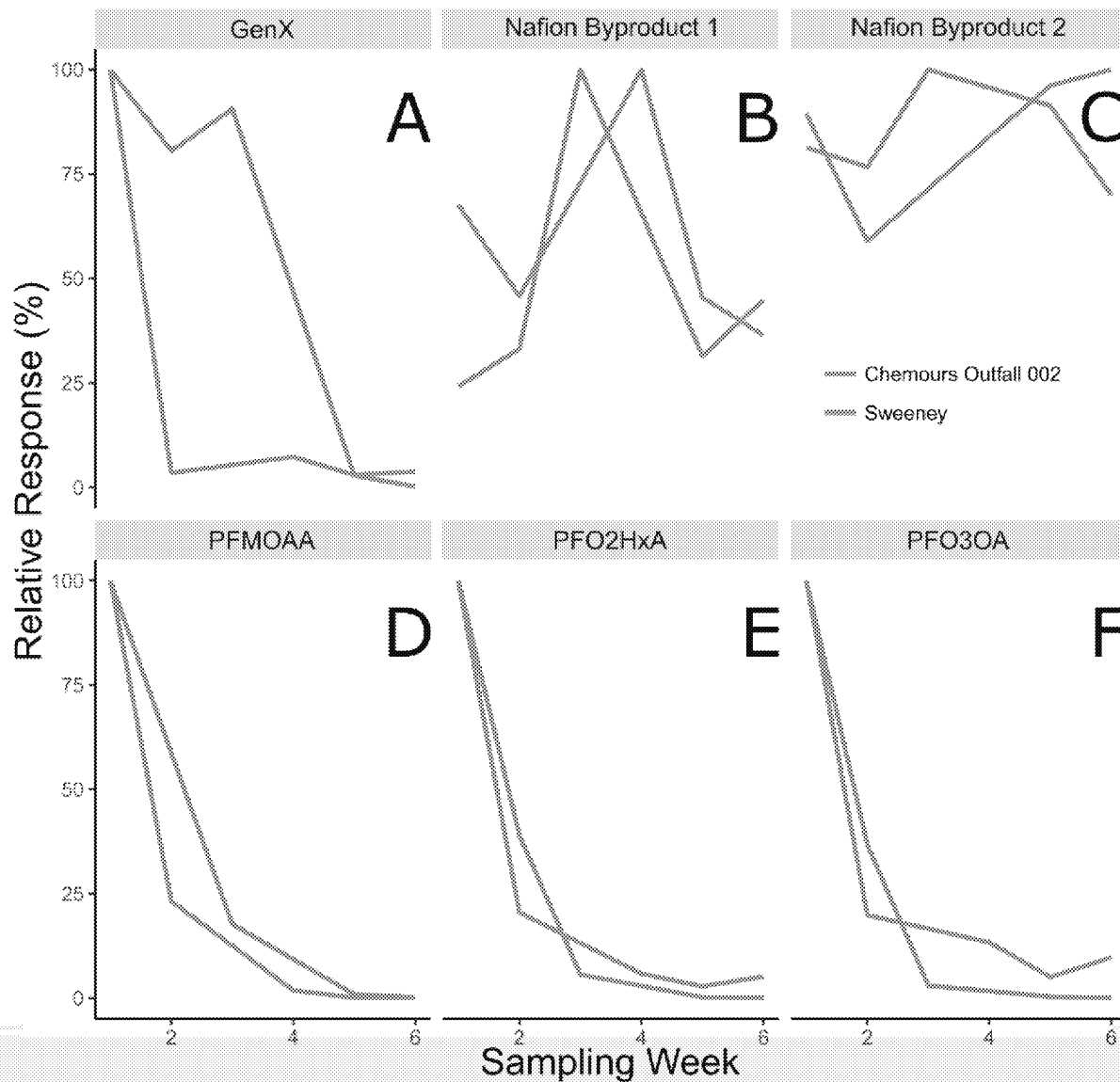


Nafion Byproduct Conc. Profiles

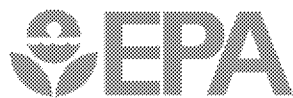




Relative Change in PFAS Conc.



- Non-targeted assessment provides a powerful means to characterize actual occurrence/exposure
- GenX and at least 3 other related compounds observed to decreased substantively across monitored watershed including finished drinking water
- GenX measured below the 140 ng/L threshold in drinking water but remains in the 70 - 95 ng/L range
- Two other “GenX-related” compounds remain elevated PFO2HxA ~ 1000 ng/L and PFO3OA ~ 700 – 800 ng/L
- Two Nafion related compounds do not show same decreasing trend as GenX-related compounds
- Nafion related compounds observed in drinking water ~ 2,000 to 4,000 ng/L range
- Other PFAS remain undescribed and will require further evaluation
- EPA Partnership / response with NC DEQ ongoing
 - Monitoring, tox testing, risk assessment, risk management



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